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Zafeiri, I.; Horridge, C.; Tripodi, E.; Spyropoulos, F.

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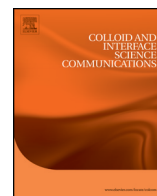
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Rapid Communication

Emulsions Co-Stabilised by Edible Pickering Particles and Surfactants: The Effect of HLB Value

I. Zafeiri ^{*}, C. Horridge, E. Tripodi, F. Spyropoulos

School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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Over the last two decades there has been an upsurge of research interest in the study of Pickering emulsions. The benefits of having particle-laden interfaces, mainly relating to prolonged emulsion stability, have been extensively reviewed [1,2]. Nonetheless, adoption of Pickering stabilisation strategies within the foods arena is still somewhat hampered due to the challenges associated with the development of Pickering structures from edible elements [3,4]. Polysaccharides and proteins are the two most commonly investigated materials when it comes to the use of particles of biological origin as stabilisers of emulsions and foams. Among semi-crystalline polysaccharides, several cellulose derivatives of interesting particle shapes have been utilised; e.g. bacterial cellulose fibres, ethylcellulose, hydroxypropyl methylcellulose phthalate and starch [5].

Hydroxypropyl methylcellulose (HPMC) is a hydrophobic cellulose derivative approved for use in foodstuffs; e.g. baked goods, sauces, dressings, and whipped toppings [6]. A chemical modification that involves addition of methyl and hydroxypropyl groups to the anhydroglucose backbone induces increased polymer hydrophobicity due to these groups. This renders the polymer interfacially active; in essence being able to adsorb to liquid-liquid interfaces and lower interfacial tension [7,8]. High hydrophobicity leads to the polymer forming aggregates within an aqueous environment, hence adopting a behaviour that resembles more that of a colloidal particle. Several studies have reported on the ability of HPMC to form and stabilise emulsions, mainly evaluating the effect of the polymer's molecular weight, degree of substitution with methoxyl groups [9] or that of its blends with other biopolymers such as β -lactoglobulin [10].

For Pickering particles acting as emulsion stabilisers, emulsion type is governed by the balance between the hydrophilic and lipophilic domains of their microstructure, in this case best described by their

wettability [11]. This is somewhat different to surfactants which have traditionally been used to stabilise emulsions, due to their inherent amphipathic character. The type of emulsion that a given surfactant species tends to facilitate forming (oil-in-water, o/w, or water-in-oil, w/o) can be primarily predicted based on its hydrophilic-lipophilic balance (HLB) value. When used in conjunction with colloidal particles, low molecular weight surfactants (even at relatively low concentrations) have the potential to provide emulsions with much lower droplet sizes compared to systems where each of these entities is used as the sole interfacial stabiliser [11]. It has been proposed that long-term storage stability in an o/w emulsion containing both a surfactant and colloidal particles is ensured via a two-part synergistic mechanism where each component has a well-defined task [11,12]. This behaviour was found to be dependent not only on the concentrations of both components but also on the type of surfactant employed [12]. Surfactant usage in the presence of colloidal particles can therefore be exploited as a means of adjusting particle wettability, and thus tailoring the emulsion's interfacial composition. The majority of work in this area has focused on mixtures of silica nanoparticles with a range of surfactant species, with studies on colloidal particles of closer association to what would be perceived as an edible Pickering structure being scarce. For example, it has been demonstrated that when cellulose ethers were mixed with anionic or double chain cationic surfactants, a time-dependent synergy was developed between the neutral polymer aggregates and the surfactant [13, 14]. Nevertheless, both these studies focused on analysing the dynamic and equilibrium adsorption behaviour of these polymeric-surfactant mixtures at the air/water interface and in the presence of electrostatic effects.

The current study investigates the impact of the surfactant's HLB value on the formation and stability of mixed-emulsifier stabilised emulsions (systems stabilised by both surfactants and Pickering particles) produced through different processing routes. In this view, o/w emulsions stabilised solely by conventional surfactants of markedly different HLB characteristics (Tween 80, PGPR) or edible colloidal particles (HPMC) or mixture of both species, were formed using different emulsification methods. For all investigated systems the achieved emulsion droplet sizes and their storage stability were assessed, and the role of the HLB value of the used surfactant on emulsion behaviour was determined.

For the stabilisation of the o/w emulsions the non-ionic synthetic surfactants Tween 80 ($HLB_{T80} = 15$, $M_{T80} \approx 1310$ g/mol) and PGPR ($HLB_{PGPR} = 1.5$, $M_{PGPR} \approx 353.51$ g/mol), which are typical o/w and w/o stabilisers respectively, were used in the study. HPMC ($M_{HPMC} \approx 86$ kDa) was employed as the edible Pickering particle

^{*} Corresponding author.

E-mail address: ixz160@bham.ac.uk (I. Zafeiri).

component. Both particle and surfactant concentrations in the investigated systems are calculated and provided as weight percentages of the overall mass of the relevant emulsion (wt%). Mixed-emulsifier stabilised emulsions were fabricated by initially dissolving the surfactant component (depending on its specific HLB value) in either the distilled water or sunflower oil phases; as such, Tween 80 was initially dissolved in the water phase while PGPR in the oil phase. HPMC was added to the surfactant solutions and was then mixed with either pure sunflower oil or distilled water to emulsify them using a high shear mixer (L5 M, Silverson, UK). These o/w emulsions were analysed as such or were further processed using an air-driven microfluidiser device (M110-S, Microfluidics, USA). Following production, all mixed-emulsifier stabilised emulsions were assessed in terms of their stability against coalescence via droplet size measurements conducted using laser diffraction (Mastersizer Hydro 2000SM, Malvern, UK). In addition, the interfacial behaviour of all systems was measured as a function of time through equilibrium interfacial tension measurements at room temperature. These were carried out in a tensiometer (K100 Krüss, Germany) using the Wilhelmy plate method.

The ability to stabilise emulsions stems from the ability to lower interfacial tension, hence the two systems were analysed as a pure particle/surfactant or as a mixture of particles and surfactant for their behaviour at the water-sunflower oil interface. Fig. 1 depicts the interfacial tension between water and oil as a function of the concentration of Tween 80 in the presence of a constant concentration of colloidal particles.

Although it is debatable whether significant differences exist, the interfacial tension profile shows some trends that are worth discussion. Fig. 1 demonstrates that HPMC particles delay the adsorption at the interface in the case of mixed systems as the values obtained at $t = 1$ s, range between the pure HPMC and Tween 80 system (13.07 mN/m and 8.27 mN/m respectively). At the initial stages of the measurement that are more related to droplet break-up and formation, the values follow the stepwise addition of surfactant (i.e. decrease when the amount of surfactant increases). Similarly to the case of hydrophilic silica particles and Tween 60 [15], the ability of a high HLB value surfactant to reduce interfacial tension is affected by the presence of colloidal particles and seems to be dependent on the amount of surfactant. More specifically, by increasing the concentration of Tween 80 in the mixed-

emulsifier systems the interfacial tension decreases significantly for low amounts (7.6 mN/m for 0.01 wt% and 6.04 mN/m for 0.1 wt%) and only slightly for concentrations above 1 wt%.

For higher concentrations of Tween 80 (≥ 1 wt%) in the mixed-emulsifier systems, the interfacial tension evolves differently and becomes even lower than solely Tween 80 after 16 min (5.6 mN/m at equilibrium), anticipating a much more efficient droplet break-up during emulsification and a subsequent droplet size decrease. This slight reduction, compared to the pure surfactant, could be attributed to the fact that the concentration of Tween 80 in the aqueous phase when HPMC particles are present, is slightly higher than Tween 80 on its own, affecting accordingly the tension at the interface. It is also possible that this behaviour is a result of a rearrangement of the stabilising species taking place at the interface. HPMC particles are potentially displaced from the interface, driven by the increase in Tween 80's concentration in the system.

This synergism between a polymeric based particle and a surfactant system has been observed before for mixtures of cellulose ethers such as ethyl(hydroxyethyl)cellulose (EHEC) or HPMC with ionic surfactants. The interaction between these two components engenders associated structures with higher surface activity than each of the entities alone [14]. These interactions have a great practical importance as, among others, reducing the total amount of surfactant is tremendously appreciated from an environmental and economic perspective [13].

The effect of a low HLB surfactant on the interfacial tension in the presence or absence of HPMC particles is shown in Fig. 2. As opposed to Tween 80, for concentrations of PGPR as low as 0.1 wt% the mixed system behaves identically or almost identically to the pure surfactant. Similar to previous observations apropos the mixture of silica particles and a w/o surfactant (e.g. lecithin) [15], HPMC particles appear to have a negligible effect on the interfacial tension, particularly at surfactant concentrations ≥ 0.1 wt%. An additional difference between Figs. 1 and 2 lies in the thermodynamic equilibrium state that, in the case of Tween 80, is not reached within the time frame of 1000 s as interfacial tension decreases continuously with time, while for PGPR it is reached directly upon adsorption of surfactant into the interface. Caused by variations in surfactants' architectural characteristics which affect how they pack at the interface, steric hindrance is what prevents or allows

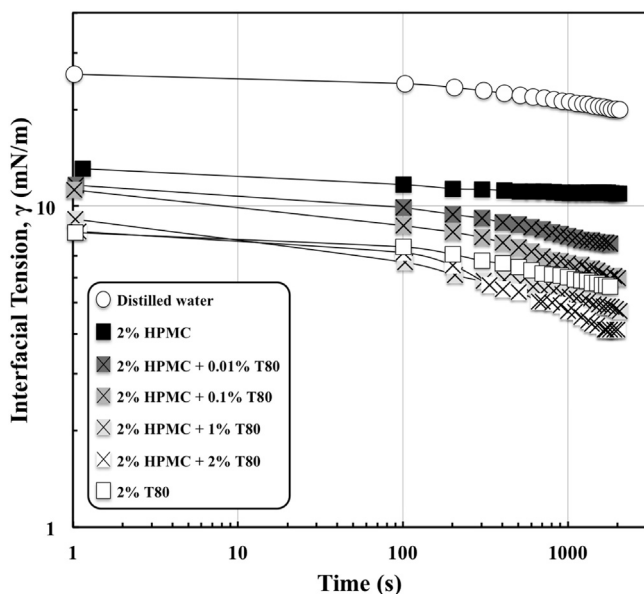


Fig. 1. Dynamic interfacial tension data as a function of a pure system containing particles or surfactant and of a mixed system containing 2 wt% HPMC and different concentrations of Tween 80. A logarithmic scale in both axes gives a better view of the time-scale of the experiment.

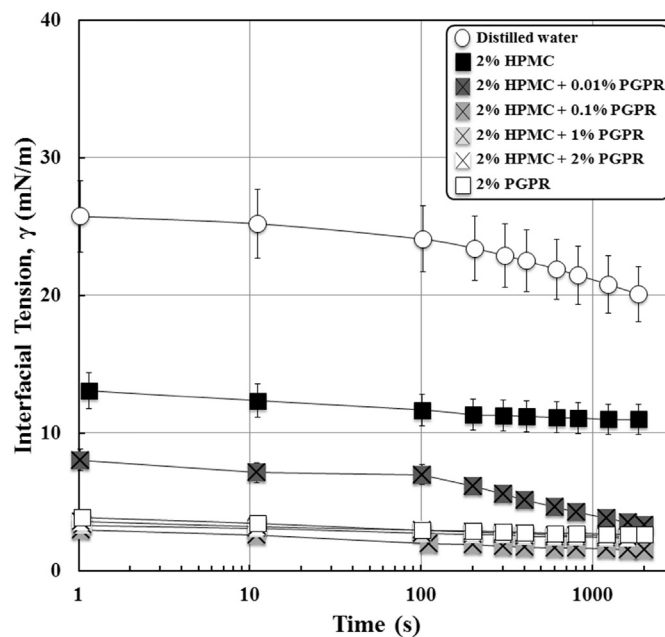


Fig. 2. Dynamic interfacial tension data as a function of a pure system containing particles or surfactant and of a mixed system containing 2 wt% HPMC and different concentrations of PGPR.

impurities in the oil phase to enter the interface and affect the behaviour [15].

Having determined the interfacial performance of different HLB value surfactants in the presence of colloidal particles, the role of these systems on the droplet size and stability of emulsions was studied next. Oil-in-water emulsions ($w_{oil} = 0.1$) were stabilised solely by either 2 wt% HPMC or 2 wt% Tween 80 and also conjointly by HPMC and various amounts of Tween 80, and were prepared by high-shear mixing (2 min at 10,000 rpm). Fig. 3 shows the generated droplet size ($D_{3,2}$) values as a function of surfactant concentration measured immediately after emulsification and after one and two weeks of storage at room temperature.

With the exception of 0.01 wt% Tween 80 in the mixed-emulsifier systems, all emulsions fabricated with the o/w surfactant in the presence or absence of Pickering particles were stable against coalescence with only minor changes in droplet size with time. Droplet sizes of particle and surfactant-stabilised emulsions showed no notable difference between them (7.7 μm and 7.1 μm following emulsification), despite the lower interfacial tension values of Tween 80 as discussed above. The balance between the competing events of droplet break-up and re-coalescence that take place during the emulsification is the one that determines the final emulsion droplet size. Tween might be able to promote droplet break-up via the reduction of the interfacial tension, but HPMC particles, as long as they breach the oil/water interface, are more efficient in reducing the coalescence rate, producing eventually similar droplet sizes.

Upon addition of Tween 80 to a 2 wt% HPMC aqueous solution, emulsions of smaller droplet sizes are produced (Fig. 3). The average droplet diameter is reduced as a function of the surfactant concentration for the entire concentration spectrum investigated, while in all cases it is significantly smaller than those in the presence of surfactants or particles alone. Importantly, the reduction in droplet size follows the same trend as the interfacial tension profile, i.e. a gradient reduction with increasing surfactant concentration.

The observed droplet size pattern comes into contrast with the behaviour reported previously for emulsions containing silica particles and o/w surfactant (Tween 60 or sodium caseinate) [12]. In that case, variations in surfactant concentration dictated the location of the particles in relation to the interface which, in turn, dictated the final droplet size. Specifically, Pichot et al. [15] identified a surfactant concentration above which there is no synergistic action between the surfactant and the colloidal silica particles, and the interfacial tension profile is

determined only by the amount of surfactant. It was argued that this behaviour is closely linked to the positioning of the particles at the emulsion interface. In our study, 0.01 wt% Tween 80 in the mixed system fulfills its role of promoting further break-up, generating smaller size droplets post-emulsification; yet this behaviour is only temporary as after 7 days the system returns back to a particle-stabilised emulsion. The fact that mixed-emulsifier stabilised emulsions of higher Tween concentrations retain their initial size after 2 weeks suggests that given the increased amount of surfactant, the tendency for droplet-droplet collision is minimised.

Having demonstrated that a high HLB surfactant enhances the functionality of these mixed systems, we sought to investigate whether such synergism persists in the case of low HLB value surface active species, e.g. PGPR. The dependency of emulsions' droplet size on the surfactant's concentration in the absence and presence of 2 wt% HPMC particles, is shown in Fig. 4 along with their evolution with storage time.

The inclusion of PGPR in the formulation affects the resulting droplet sizes considerably, albeit in a different manner to Tween 80 systems. Although PGPR on its own initially seems to encourage droplet disruption to the same extent as Tween 80 (Figs. 1, 2), it eventually fails to render the droplets stable against coalescence and leads to a phase-separated system. This is usually the case as emulsifiers of low HLB values will tend to stabilise w/o rather than o/w emulsions. However, when used in combination with HPMC particles and at low concentrations of PGPR, a significant benefit arises; in fact, a 22.8% and a 35.6% decrease in droplet size is observed when small concentrations of the surfactant (0.01 wt% and 0.1 wt% respectively) are used together with 2% cellulose particles. As Fig. 4 shows, at concentrations of PGPR up to 1 wt%, droplet sizes decrease and are overall slightly larger than HPMC-Tween 80 stabilised ones. For high PGPR amounts (i.e. ≥ 1 wt%), there is no further benefit observed through subsequent surfactant addition, and o/w emulsions produced are not stable, with large droplets appearing over time (Fig. 4).

The mechanisms that lie behind the adsorption of particles and surfactants to the interface during the emulsification process could account for this behaviour. In emulsions stabilised by a mixture of silica particles and lecithin, SEM analysis of the emulsion microstructure revealed that there is no dependency between the surfactant concentration and the acquired droplet size [12]. Emulsions were stabilised by the particles (Pickering stabilisation) and any increase on lecithin's concentration did not lead to their desorption from the interface. Nevertheless, this is not entirely true with our system as at 2 wt% PGPR concentration, a small deposit of particles was observed at the bottom of the vessel.

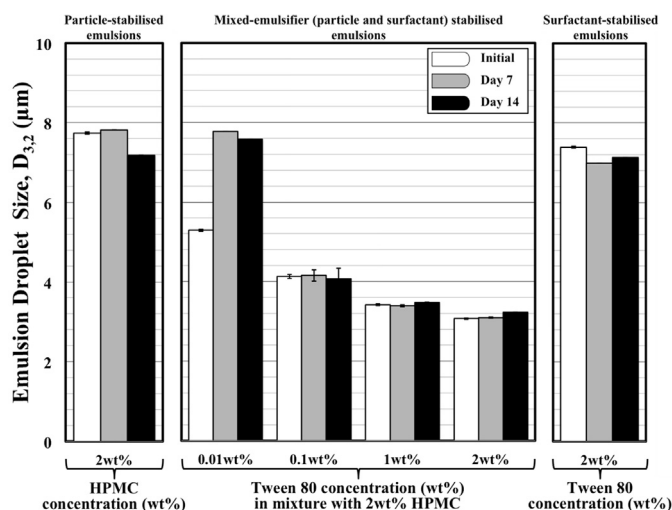


Fig. 3. Average droplet sizes of emulsions stabilised by solely HPMC, solely Tween 80 and different concentrations of Tween 80 in the presence of 2 wt% HPMC over time and as a function of the surfactant concentration. Where not visible, error bars are smaller than symbols.

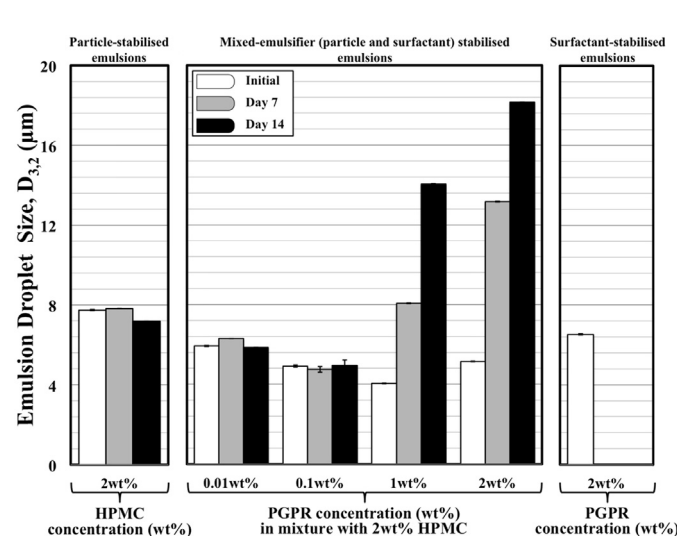


Fig. 4. Average droplet sizes of emulsions stabilised by solely HPMC, solely PGPR and different concentrations of PGPR in the presence of 2 wt% HPMC as a function of the surfactant concentration.

One could argue that this was the result of particles' displacement, which also explains the more surfactant-dominated performance as seen in Fig. 4. Further experiments with different concentrations of PGPR and visualisation of the emulsions' surface would shed some light on the exact mechanism(s) taking place.

A comparison between Figs. 3 and 4 suggests a far superior performance of PGPR than Tween, at very low concentrations. An important factor is the surfactants' HLB value and their molecular architecture. We hypothesise that a low HLB value surfactant has a stronger tendency than a high HLB value one to shift the hydrophobicity of HPMC at lower concentrations and therefore render an o/w emulsion more stable. Essentially, PGPR having more lipophilic sites than Tween has more chances to bind to the somewhat hydrophobic particles through hydrophobic interactions and increase the hydrophilic character, making them more stable in the aqueous phase. In addition, the molecular geometry of a surfactant determines factors such as the critical packing parameter, which in turn affects interfacial curvature. The highly lipophilic PGPR, having an area per chain larger than the hydrophilic head group, has a tendency to curve around water. This surfactant configuration does not favour long-term stabilisation of o/w emulsions. This change in curvature angle could also be responsible for the larger droplet sizes of PGPR as opposed to Tween 80 mixed stabilised emulsions.

The effect of processing method, and in particular how the effect of surfactant's HLB value would be altered by using an emulsification process of significantly higher energy input was investigated next. A series of o/w emulsions were produced with 10 wt% sunflower oil and the mixtures HPMC-Tween 80 and HPMC-PGPR at the same concentration regimes as the emulsions produced using a high-shear mixer. Droplet size data for the two types of mixed systems at 1000 bar and for one pass as measured straight after emulsification and after one week storage at room temperature are shown in Fig. 5.

Fig. 5 clearly suggests that the exertion of high pressures in both systems induced a dramatic decrease in the generated droplet sizes. A single pass through the microfluidiser was sufficient to produce submicron emulsion droplets with a size range of 200–400 nm in both cases. The trends observed are quite similar to the ones acquired by the high shear device, however for both surfactants a more or less constant size is reached for concentrations above a specific value. Long-term stability was also conferred to the systems in a way rather similar to the stability of emulsions produced with a high-shear device.

In terms of the mixed systems containing the high HLB value surfactant, at low concentrations of Tween 80 (0.01 wt%), the effect of the

surfactant component seems to be negligible. Indeed, the resulting emulsion has a mean droplet size of 0.378 μm which is even higher than the HPMC particles on their own (0.338 μm). A gradual increase in the amount of Tween leads to a 58% decrease in the droplet size which then almost reaches a plateau up until the highest concentrations. The mixed HPMC and PGPR systems behaved analogously. Unlike the emulsions produced on the high shear mixer, over the same surfactant concentration range, droplet sizes continue to decrease with subsequent addition of PGPR, steeply for concentrations up to 1 wt% and at a less rapid rate for 2 wt%. Fig. 5 obviously illustrates the absence of droplet size dependency on surfactant concentration for concentrations higher than 0.1 wt% and 1 wt% for the Tween and PGPR mixed systems respectively. This pattern variation probably implies a different location of particles and surfactants in the bulk and at the interface, dictated by the distinct shear regime to which the emulsions are subjected inside the microfluidiser.

The intense disruptive forces applied on the system in the microfluidiser result in an increased specific surface area. The increased interfacial area of the emulsions compared to that produced on a high shear mixer will require higher concentrations of surfactant available to stabilise and prevent coalescence. Upon increasing the surfactant concentration in a mixed-emulsifier stabilised emulsion, it begins to dominate the system at much lower concentrations compared to a high shear device, as more of it will be used to cover the increased interfacial area.

In summary, this work advances the current understanding on mixed-emulsifier stabilised emulsions, by specifically focusing on the influence of the (employed) surfactant's HLB value. This study demonstrates that addition of small amounts of surfactant can enhance the functionality of an edible Pickering particle component in terms of the emulsion droplet sizes that are generated and the stability to coalescence that is induced. The findings provided here offer strong evidence that these emulsion features are directly influenced by the concentrations of the two components and more importantly by the surfactant's HLB value. In addition, the co-stabilisation approach reported here is shown to provide stable oil-in-water emulsions even in the presence of surfactants of low HLB value (conventionally used as stabilisers of water-in-oil emulsions). Furthermore, the impact observed persists across different processing conditions (i.e. at relatively low and high shear environments). The observed synergy between the two interfacial entities is foreseen to provide applications in a wide range of commercial settings where optimisation of emulsions structure, utilisation of sustainable interfacial species and/or reduction of surfactant content are required.

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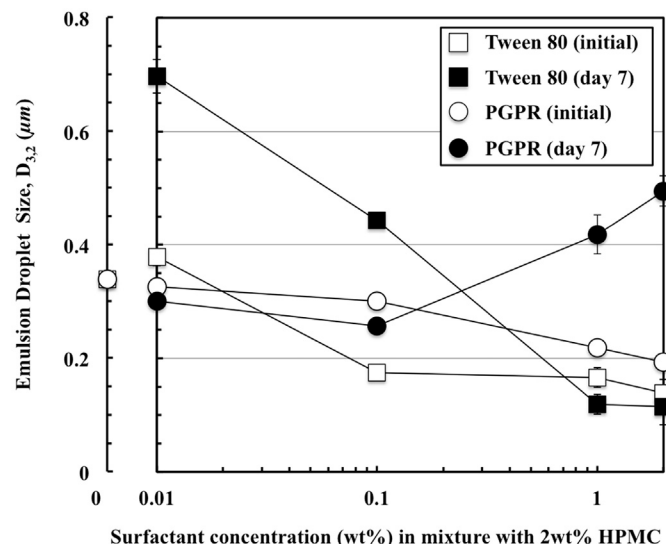


Fig. 5. Average droplet sizes of 10% o/w emulsions stabilised by mixed HPMC-Tween 80 and HPMC-PGPR (2 wt% particles & 2 wt% surfactant) produced at 1000 bar using the microfluidiser, as a function of the surfactant concentration.

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